Quadratic Magnetoelectric Effect and Magnetic Field Induced Pyroelectric Effect in Multiferroic $BaMnF_4$

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The experimental studies of magnetoelectric effects in pulse magnetic field up to 250 kOe and their theoretical analysis on the basis of magnetic symmetry consideration are carried out. It is shown that the nonvanishing components of quadratic magnetoelectric effect tensor corresponding to the electric polarization along b- and -axes point out the triclinic distortion of the crystal symmetry. Anomalous temperature dependence of magnetically induced polarization $P_a(H_b)$ testifies to the magnetically induced pyroelectric effect. The torque curves measurements show the deflection of the spin orientation from the b-axis at 9 degrees of arc.

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The fluoride $BaMnF_4$ is a classical ferroelectromagnet (in modern terms multiferroic) and it has been the subject of intensive research for some decades (see, for example, the review [1] and reference therein, and also later publications [2-10]). It belongs to the family of isomorphic compounds of general formula $BaMF_4$, where $M = Mn, Fe, Co, Ni, Mg, Zn$, which are paramagnetic at room temperature. Their crystal structure is described by the orthorhombic space group $A2_1am$ (a=5.9845, b = 15.098, c = 4.2216) in international notation (or C_{2v}^{12} in Schoenflies notation). The $A2_1am$ group includes twofold 2_1 screw axis parallel to the a-axis with the shift of $a/2$, the glide symmetry plane a perpendicular to b-axis with the shift along a-axis at $a/2$, two mirror planes m perpendicular to the c-axis, located at $z = 0, c/2$ and corresponding translations. In contrast to the other fluorides the $BaMnF_4$ is pyroelectric, besides the ferroelectric and antiferromagnetic phase transition ($T_C \approx 1113\ K, T_N \approx 25\ K$ [10-12]) it has structural phase transition at $T_0 \approx 250\ K$ into

incommensurate monoclinic phase, that retains at low temperatures. In $BaMnF_4$ spontaneous electric polarization $\mathbf{P}_s \parallel \mathbf{a}$. Symmetry allows the existence of antiferroelectric ordering along b-axis, but forbids one along c-axis.

Structural phase transition into the incommensurate phase at $T_0 = 250\ K$ in $BaMnF_4$, is described by the wave vector $\mathbf{q} = (\mu/a, 0.5, 0.5)$, where $\mu = 0.39$. That means the size of the primitive cell doubles in the bc-plane and incommensurate structure along the a-axis with a period $a/\mu = 15\AA$ occurs. It is established, that this transition at $T_0 = 250K$ is ferroelastic one [2,3].

Magnetoelectric properties of the $BaMnF_4$ are still not completely understood. For example the symmetry allows linear magnetoelectric effect and ferroelectrically induced weak ferromagnetism [1] but they are not observed experimentally (presumably their volume averaged values are zeroed out due to the existence of incommensurate structure). Quadratic magnetoelectric effect though observed [2] was measured only for polarization along -axis, while the measurements of other components can serve as sensitive indicator of symmetry distortions. As in $BaMnF_4$ ferroelectric and ferromagnetic ordering coexist, the heat induced pyroelectric and magnetocaloric effects, as well as magnetoelectric effect, mediated by heating, are possible.

In this paper the magnetoelectric dependencies in high magnetic field up to 250 kOe at various direction of polarization and magnetic field, as well as torque curves in static fields up to 12 kOe are measured for the first time in single crystal $BaMnF_4$ in the temperature range 4.5-150 . They are interpreted on the basis of crystal and magnetic symmetry as well as magnetic structure and magnetic field induced phase transitions. The anomalous temperature dependence of magnetically induced polarization $P_a(H_b)$ is explained by magnetocaloric and pyroelectric effects.

1.Experiment The magnetic field induced electric polarization measurements showed that longitudinal quadratic magnetoelectric effect is maximum along a-axis of the crystal ($\beta_{11} \approx 1.6 \cdot 10^{-19} sA^{-1}$ at $4.5\ K$), along which spontaneous polarization is directed (fig. 1). The transversal electric polarization $P_b(H_a)$ was also proportional to the square of magnetic field ($\beta_{21} \approx 1.4 \cdot 10^{-20} sA^{-1}$ at $30\ K$), lowering with the growing temperature (fig. 2). The longitudinal electric polarization dependence $P_c(H_c)$ (fig. 3) has somewhat intricate character and differers qualitatively from $P_a(H_a)$. At temperature 4.5 K there was maximum of negative electric polarization in the field ~50 kOe, followed by decrease of absolute value

and sign reversal at 200 kOe. At higher temperatures up to $T_N = 25\ K$ the character of the dependencies $P_c(H_c)$ was similar, and maximum of electric polarization shifted in the region of higher fields ~ 100 kOe. Complicated character of $P_c(H_c)$ dependence points out the transformation of magnetoelectric interactions that possibly related to the magnetic structure changes in high magnetic field, particularly due to the spin modulated structure suppression as it was observed in $BiFeO_3$ [13]. In the magnetic field oriented along b-axis the anomalies of magnetoelectric effect at spin-flop phase transition were observed ($H_{SF} \approx 10$kOe). In fig. 4 the magnetic field dependencies of the longitudinal magnetoelectric effect $P_b(H_b)$ are shown. The jump of electric polarization at $H \sim 10$ kOe is followed by quadratic magnetoelectric dependence, that is related to the change of the symmetry from 2' to 2. At H——b along - and - axes (fig. 5, 6) the jumps of electric polarization at H≈ 10 kOe were observed. The transversal electric polarization along the c-axis increased with temperature decrease, while the one along the a-axis decreased, vanishing at =4,5K.

The torque curves in the bc-plane are shown in figure 7. Below Neel temperature the distinct anomalies (jumps) at magnetic field orientation $90 \pm 9°$ to b-axis ($\varphi \approx 150°$ in the figure) take place.

2. Discussion. In the high symmetry orthorhombic phase ($2mm$) of $BaMnF_4$ the linear magnetoelectric effect is apparently absent, and the quadratic effect is expressed by formula

$$P_i = \beta_{ijk} H_j H_k, \tag{1}$$

where the magnetoelectric tensor of the 3-rd rank is [14]

$$\begin{pmatrix} \beta_{11} & \beta_{12} & \beta_{13} & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & \beta_{26} \\ 0 & 0 & 0 & 0 & \beta_{35} & 0 \end{pmatrix}. \tag{2}$$

The coefficients β_{nm} are related to the 3-rd rank tensor components by standard rule:

$$\beta_{in} = \beta_{ijk}\,(jk \to n = 1, 2, ..., 6).$$

It is believed that the structural phase transition at $T = 250\ K$ is the transition to the incommensurate improper ferroelastic phase with the averaged monoclinic symmetry ($P2_1$)[2, 3]. The distortion of original orthorhombic structure in the low temperature phase is small and can be characterized by an angle $\alpha \backsim 10^{-2}$[2]. It is natural to assume the angle α

as a small parameter of theory, characterizing the change of physical values at the phase transition from orthorhombic to monoclinic phase.

In monoclinic phase the components of magnetoelectric tensor $\beta_{14}, \beta_{25}, \beta_{36}$ become nonvanishing. Obviously, their values should be proportional to α. Similarly, the corresponding changes of nonzero components (2) are also proportional to α, i.e. $\Delta\beta_{11}/\beta_{11} \backsim \alpha$ etc.

In accordance with [2], in the $BaMnF_4$ $\beta_{11} = 1.1 \cdot 10^{-19} sA^{-1}$, $\beta_{13} = -1.6 \cdot 10^{-19} sA^{-1}$, that agrees well with the results of our measurements ($\beta_{11} = 1.6 \div 0.8 \cdot 10^{-19} sA^{-1}$ in the temperature range $4.2 \div 15$ K) and is close to the corresponding coefficients in $BiFeO_3$ ($\backsim 10^{-19} sA^{-1}$ at 4.2 K [15]), though somewhat lower than in $PbFe_{0.5}Nb_{0.5}O_3$ ($10^{-17} - 10^{-18} sA^{-1}$ at 15)[16] and $NiSO_4 \cdot 6H_2O$, ($10^{-17} sA^{-1}$ at 4.2 [17]). There are no data about other components of β_{ijk} in $BaMnF_4$ in literature. Authors [2] carried out the measurements of the quadratic magnetoelectric effect of $BaMnF_4$ in the crystal planes ac and bc, the jump of electric polarization of unknown nature was observed that, probably, hindered from determining β_{xyy} and β_{xyz}.

It is worth noticing that according to [2], in crystal with monoclinic symmetry (class 2, with 2-fold axis along a-axis) the components of electric polarization p_y and p_z should be zero if external field is directed along crystal axes. However the group 2, assumed in [1-4] as an averaged symmetry of the $BaMnF_4$ at $T < T_0$, is somewhat approximated. Indeed, as the crystallographic structure in the $BaMnF_4$ at $T < T_0$ is incommensurate along a-axis, the element 2 is obviously violated [1]. Strictly speaking the averaged symmetry should lower to triclinic, in which all elements of the matrix (2) are nonvanishing [1]. Of course the difference of the "triclinic" tensor β_{ijk} from the "monoclinic" (2) in this case is minor with the small parameter $\sim (a/\lambda)\alpha^{1/2}$, where λ is the wavelength of incommensurate modulation, a is the lattice constant along the a-axis.

Let us consider from this point of view the experimental data (Fig.2,4,6). Indeed, at $T < T_0$ the measured values of the components $\beta_{21}, \beta_{24}, \beta_{34}$ are at least an order smaller than β_{11} (Fig.1) that is naturally explained by the smallness of triclinic distortion.

At $T < T_N$ the new features arise in magnetoelectric behavior related to the magnetic order and transformation of magnetic structure in external field. Let us consider in more detail the ground state of the crystal in low symmetry phases in terms of magnetic and antiferromagnetic vectors M and L. Neutron diffraction studies provide with contradictory information about the antiferromagnetic structure L. According to [10] vector $L \| b$-axis,

while in [11,12] the L-vector lies in bc-plane at the angle $\sim 9^\circ$ to b-axis.

Our measurements of torque curves (fig.7) testify to the deflection from b-axis, the angles at which the anomalies (jumps) observed are shifted from the middle position at the angles $\pm 9^\circ$. These jumps can not be explained by 180° reorientation of weak ferromagnetic moment M along c-axis that was introduced in [1,12,18], otherwise the weak ferromagnetic moment would reorient from parallel to antiparallel position with respect to the magnetic field that is unlikely. Qualitatively the torque curves at $H < H_{SF}$ can be explained by existence of four (effectively two) phases with the antiferromagnetic vector direction at $\pm 9^\circ$ to b-axis and phase transition between them. However the quantitative description of the torque curves requires taking into account the antiferromagnetic domains that is beyond the scope of this paper.

Thus the magnetic structure in the ground state takes the form: $\mathbf{L} = (\mathbf{0}, \mathbf{L_y}, \mathbf{L_z})$, where $(L_z/L_y) = \tan\psi$, where $\psi = 9^o$, $\mathbf{M} \approx \mathbf{0}$. This small deflection from b-axis can be interpreted as the consequence of "monoclinic" contribution $K_{yz}L_yL_z$ into anysotropy energy. The value K_{yz} is, obviously, proportional to the monoclinic distorsion of the structure at $T < T_0$, i.e. $|K_{yz}/K_{rhomb}| \sim \alpha$, where K_{rhomb} is characteristic value of "orthorhombic" contribution to the magnetic anysotropy.

In magnetic field the transformation of antiferromagnetic structure occurs, i.e. spin-flip and spin-flop transitions (depending on the direction of external magnetic field with respect to original orientation of antiferromagnetic vector). In zero approximation on parameter α the ground state magnetic structures can be presented by formulae:

$$\mathbf{H} = (H, 0, 0)$$

$$\mathbf{M} = (\chi_\perp H, 0, 0), \mathbf{L} = (0, L_y, 0),$$

$$\mathbf{H} = (0, H, 0)$$

$$\mathbf{M} = (0, \chi_\parallel H, 0), \mathbf{L} = (0, L_y, 0), H < H_{SF},$$

$$\mathbf{M} = (0, \chi_\perp H, 0), \mathbf{L} = (0, 0, L_z), H > H_{SF},$$

$$\mathbf{H} = (H, 0, 0)$$

$$\mathbf{M} = (\chi_\perp H, 0, 0), \mathbf{L} = (0, L_y, 0),),$$

where $\mathbf{M}$ is the magnetization, $\chi_{\perp}, \chi_{\|}$ are perpendicular and parallel susceptibility of the material, H_{SF} is the spin flop field ($H_{SF} \sim 10^4$ Oe in $BaMnF_4$ [2]). Taking into account the aforementioned monoclinic contribution into magnetic anisotropy would bring us out of the zero approximation on α and would lead to more bulky formulae but would not change the qualitative picture of the phenomenon.

In those cases when magnetic field is directed along a and c - axes of the crystal, the magnetic field induced components of electric polarization $\Delta p_i, i = x, y, z$ can be described on the basis of the same simple symmetry consideration as in (1):

$$\Delta p_i = a_i M_i^2 + b_i L_y^2 \sim H^2, \tag{4}$$

where a_i, b_i, are the coefficients of series expansion. It agrees qualitatively with the behaviour of the magnetoelectric curves in figures 1-3.

The different situation is at $\mathbf{H} = (0, H, 0)$. The spin flop in Mn-ions system is accompanied by the jumps of antiferromagnetic vector components and magnetization. The value of the jump is a maximum at $T \to 0K$ and tends to zero 0 at $T \to T_N$, where T_N is Neel temperature. According to (4), the jumps of electric polarization should copy this behavior. At figures 4 and 6 the jumps of Δp_y, Δp_z are clearly seen and their temperature dependences agree qualitatively to the described scheme.

However, the electric polarization Δp_x demonstrates counter intuitive behaviour (fig. 5). At $T \to 0\ K, H \| b$ the jump Δp_x is vanishing and increase at $T \to T_N$. Note also that absolute values of the electric polarization Δp_x is substantially larger than y and z components.

The probable reason for such an unusual behavior of $p_x(H)$ can be the result of pyroelectric effect caused by magnetocaloric heating of the $BaMnF_4$ sample in pulse magnetic field. Indeed, the pyroeffect is determined in this case:

$$\delta p_x = P_0\ c\ \delta T,$$

where P_0 is the value of spontaneous electric polarization, c is the constant, that depends on crystallographic parameters of the lattice and thermal expansion tensor components (see [19], for example). The value δT is determined by magnetocaloric effect:

$$\delta T = c_H^{-1} \frac{\partial M_H}{\partial T} \Delta H,$$

where c_H is the heat capacity at constant field, M_H is the projection of the magnetization on magnetic field direction, ΔH is the magnetic field increment. In figure 8 the temperature dependence of $\frac{\partial M_H}{\partial T}$ is shown, that qualitatively corresponds to the measured anomalies in $p_x(H,T)$ at $T < T_N$.

It is worth noticing that mentioned mechanisms do not exhaust the whole range of possibilities of magnetically induced electric polarization appearance in $BaMnF_4$, that possess incommensurate ferroelastic structure. The full picture includes piezoelectric effect induced by magnetostriction, and flexoelectric response, that appears in spatially modulated incommensurate structure under the influence of magnetostrictive deformations.

The first one, the piezoelectric response, is determined as

$$\delta P_\alpha^{piezo} = C_{\alpha\beta\gamma}\ \varepsilon_{\beta\gamma}(H),$$

where $\varepsilon_{\beta\gamma}$ is the tensor of magnetostriction deformation, $C_{\alpha\beta\gamma}$ is the tensor of piezoelectric coefficients.

The flexoelectric response is determined by formula [19]:

$$\delta P_\alpha^{flexo} = f_{\alpha\beta\gamma\delta}\frac{\partial^2 r_\beta(H)}{\partial x_\gamma \partial x_\delta},$$

where $\frac{\partial^2 r_\beta}{\partial x_\gamma \partial_\delta}$ is the derivative of distortion tensor (the existence of incommensurate structure in the $BaMnF_4$ evidences strogly the nonvanishing of the derivative), $f_{\alpha\beta\gamma\delta}$ is the tensor of flexoelectric coefficients.

We do not aim to make the detailed analysis of the later mechanisms; its contribution to the observed polarization should be smaller than quadratic magnetoelectric and pyroelectric effects, but they can be responsible for irregularities of magnetoelectric dependencies (Fig. 2,3).

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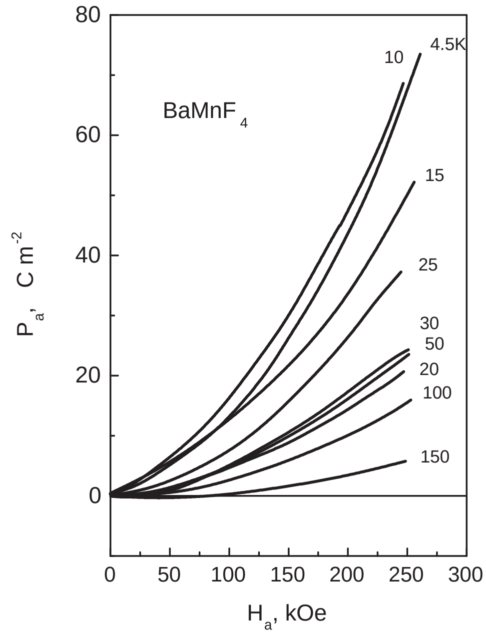

FIG. 1: Magnetoelectric dependencies $P_a(H_a)$ in pulse field at various temperatures

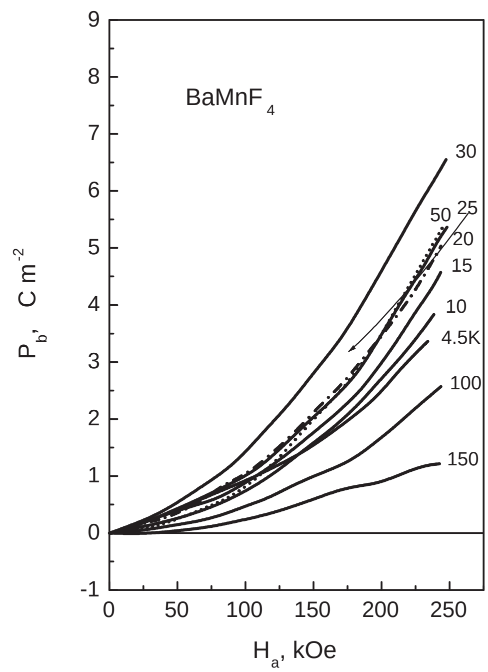

FIG. 2: Magnetoelectric dependencies $P_b(H_a)$ in pulse field at various temperatures

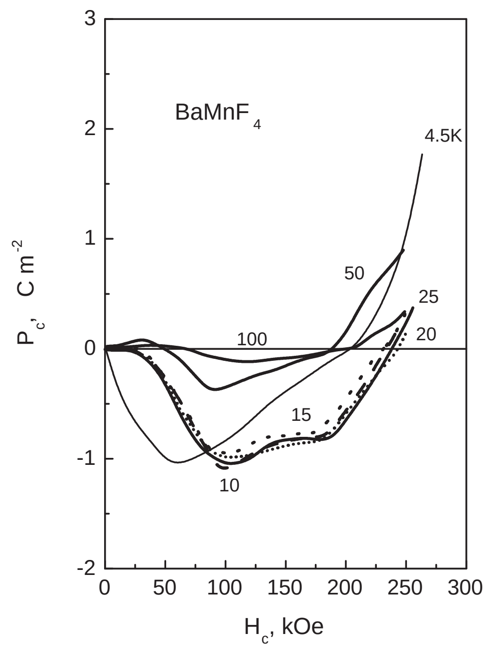

FIG. 3: Magnetoelectric dependencies $P_c(H_c)$ in pulse field at various temperatures

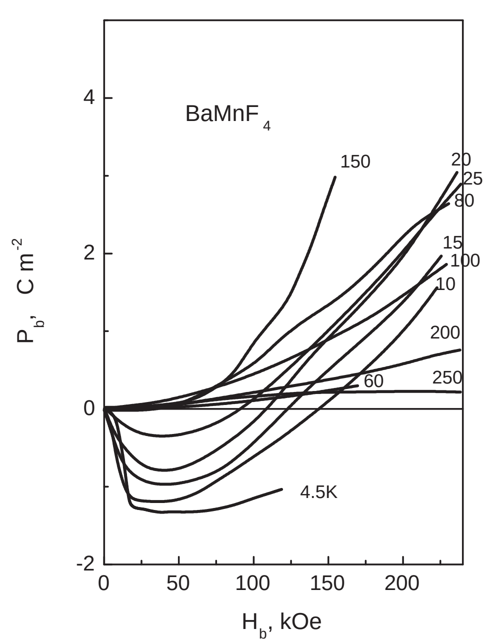

FIG. 4: Magnetoelectric dependencies $P_b(H_b)$ in pulse field at various temperatures

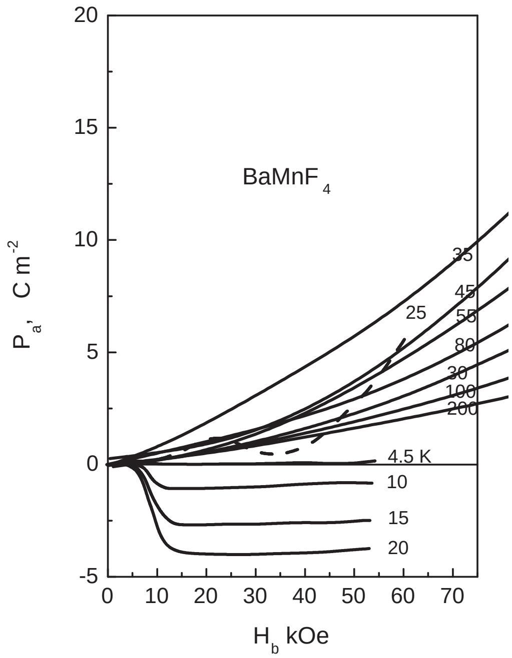

FIG. 5: Magnetoelectric dependencies $P_a(H_b)$ in pulse field at various temperatures

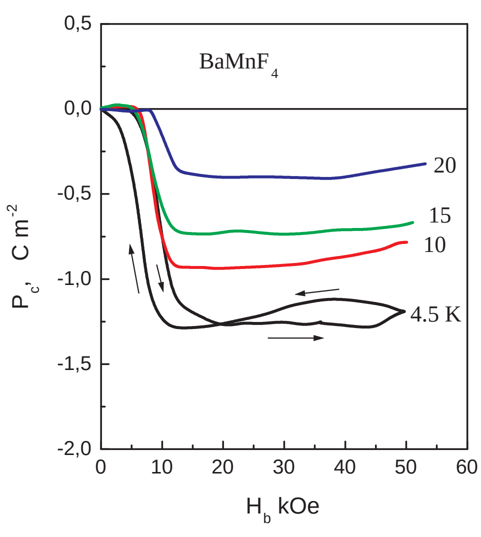

FIG. 6: Magnetoelectric dependencies $P_c(H_b)$ in pulse field at various temperatures

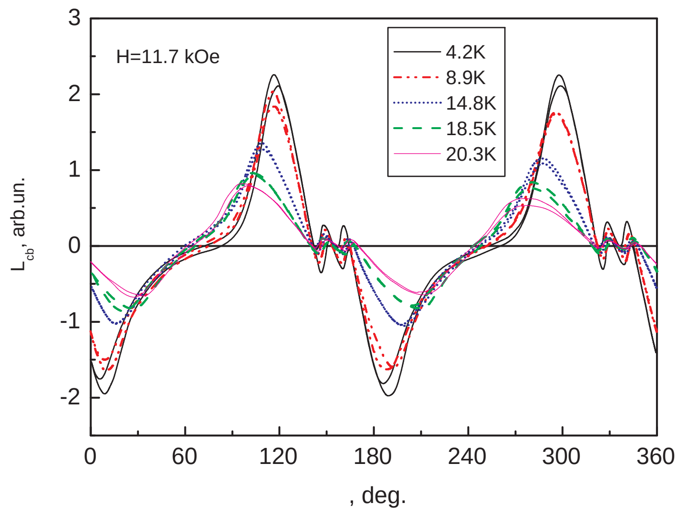

FIG. 7: Torque curves at various temperatures in static magnetic field $H < H_{spinflop}$

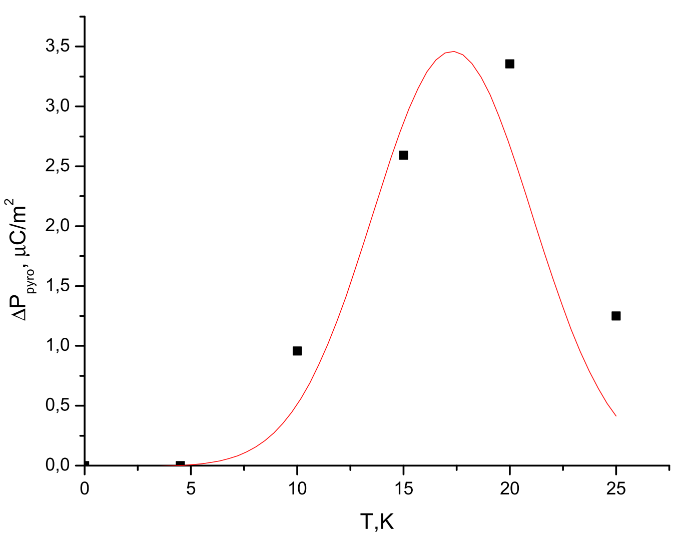

FIG. 8: The schematic curve $\frac{\partial M_H}{\partial T} = \frac{\partial \chi(T)}{\partial T} \Delta H$ (line), and magnetoelectric anomalies (points)